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(71) Applicant (for all designated States except US): EXXON CHEMICAL PATENTS, INC. [US/US]; 5200 Bayway Drive, P.O. Box 2149, Baytown, TX 77522 (US).			
(71) Applicant (for GB only): EXXON CHEMICAL LIMITED [GB/GB]; 4600 Parkway, P.O. Box 122, Fareham, Hants PO15 7AP (GB).			
(71) Applicant (for US only): VAN DEN BERGE, Jannetje, M. (legal representative of the deceased inventor) [NL/NL]; Fazantenlaan 26, NL-3233 BB Oostvoorne (NL).			(74) Agents: DARBY, David, Thomas et al.; Abel & Imray, 20 Red Lion Street, London WC1R 4PQ (GB).
(72) Inventor: VERDUIJN, Johannes, P. (deceased).			
(72) Inventors; and			
(75) Inventors/Applicants (for US only): MERTENS, Machteld, M. [BE/BE]; Beringstraat 72, B-3190 Boortmeerbeek (BE). MORTIER, Wilfried, J. [BE/BE]; Diestse Steenweg			
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(54) Title: CRYSTALLINE MOLECULAR SIEVES			
(57) Abstract A colloidal suspension of LEV structure type crystalline molecular sieve, making the suspension by washing smaller crystallites from a previously found solid LEV product, and using the suspension as seeds in further crystalline molecular sieve syntheses.			

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CRYSTALLINE MOLECULAR SIEVES

This invention relates to molecular sieves and processes
5 for their manufacture. More especially it relates to
processes in which synthesis mixtures are seeded to control
process conditions and product characteristics, to
compositions for providing seeds in such processes, and to
methods of obtaining such compositions.

10 It is well known that seeding a molecular sieve
synthesis mixture frequently has beneficial effects, for
example in controlling the particle size of the product,
avoiding the need for an organic template, accelerating
synthesis, and improving the proportion of product that is of
15 the intended structure type.

Colloidal seeds have proved especially effective, as
described in International Application No. WO 97/03019,
03020, and 03021, and EP-A-753 483, 753 484, and 753 485.
Whereas procedures for the preparation of colloidal

20 dispersions of certain structure types have been described in
the above-mentioned references, and similar procedures are
effective in the preparation of colloidal dispersions of
crystalline molecular sieves of other structure types, these
procedures have proved ineffective in the preparation of
25 colloidal dispersions of certain further structure types,
especially LEV.

As used in this specification, the term "structure type"
is used in the sense described in the Structure Type Atlas,
Zeolites 17, 1996.

30 It has now been found that colloidal LEV may be produced
by a completely different method, and that a colloidal LEV
structure type crystalline molecular sieve, especially in the
form of a colloidal dispersion, has valuable properties in
seeding the manufacture of crystalline molecular sieves.

The present invention provides, in a first aspect, a colloidal suspension of a LEV structure type crystalline molecular sieve.

The present invention also provides a method for
5 preparing a colloidal suspension of LEV by synthesizing a LEV structure type crystalline molecular sieve by treatment of an appropriate synthesis mixture, separating the product from the synthesis mixture, washing the product, and recovering the resulting wash liquid.

10 Without wishing to be bound by any theory, it is believed that the LEV produced by a conventional LEV synthesis comprises LEV particles of greater size, normally in excess of 1 μ m, intermixed with particles of colloidal size, which are separable from the larger particles by
15 conventional water-washing processes. It has been observed that while the first wash water may sometimes be clear, and may contain no or very few colloidal particles, the second or subsequent wash water is not clear, and has a measurable solids content. The resulting wash waters are colloidal
20 suspensions or dispersions of LEV crystallites, which have considerable utility as sources of seeds in crystalline molecular sieve manufacture. (If desired, the dispersions may be made more concentrated before use.)

The colloidal LEV seeds of the invention and produced by
25 a method according to the invention are especially suitable for use in syntheses to produce crystalline molecular sieves of the LEV, FER, MOR, ERI/OFF, MAZ, OFF, ZSM-57, and CHA structure types. Examples of CHA materials are Chabasite and the phosphorus-containing molecular sieves SAPO-, AlPO-,
30 MeAPO-, MeAPSO-, ElAPSO- and ElAPO -37 and especially the corresponding -34 materials. In these formulae, El represents magnesium, zinc, iron, cobalt, nickel, manganese, chromium or mixtures of any two or more such elements. Examples of MAZ materials include mazzite, zeolite omega, and ZSM-4.

Colloidal LEV structure type seeds may also be used in the synthesis of phosphorus-containing crystalline molecular sieves, e.g., SAPO-, AlPO-, MeAPO-, MeAPSO-, ElAPSO- and ElAPO- materials, of the LEV structure type, e.g., the -35 materials. (Where a material is referred to as, for example, a SAPO material, this terminology includes the possibility that additional elements may be present, either in the framework or otherwise). LEV structure type zeolites may also be prepared using the colloidal seeds of the invention, for example Levyne, ZK-20, NU-3 and ZSM-45.

As used herein, the term "colloidal", when used of a suspension, refers to one containing discrete finely divided particles dispersed in a continuous liquid phase and preferably refers to a suspension that is stable, in the sense that no visible separation occurs or sediment forms, in a period sufficient for the use intended, advantageously for at least 10, more advantageously at least 20, preferably at least 100, and more preferably at least 500, hours at ambient temperature (23°C). The maximum size of the particles for the suspension to remain stable (peptized) will depend to some extent on their shape, and on the nature and pH of the continuous medium, as well as on the period during which the suspension must remain usable. In general, the maximum dimension will be 1µm, advantageously 500, more advantageously 400, preferably 300, more preferably 200, and most preferably 100, nm. The particles may be spherical, or of other shapes. Where particles are other than spherical, the dimension referred to is their smallest dimension.

The minimum dimension is such that the particles do not dissolve or re-dissolve in the medium, and for crystallinity they must contain at least a small plurality, advantageously at least two, preferably four, unit cells of the crystal. The minimum particle size is in general 5, advantageously 10, and preferably 20, nm. Mean particle sizes are generally in

the range 5 to 1000, advantageously 10 to 300, more advantageously 10 to 200, and preferably 20 to 100, nm. Advantageously at least 50%, more advantageously at least 80%, and more preferably at least 95%, by number, of the
5 particles are greater than the given minima, smaller than the given maxima, or within the given ranges of particle size. Measurements of particle size may be effected by electron microscopy, for example using a Philips SEM 515 unit.

As indicated above, the colloidal seeds of the invention
10 have utility in the manufacture of a variety of crystalline molecular sieves by incorporating the seeds as a component of a synthesis mixture. They are advantageously incorporated in the synthesis mixture in the form of a suspension, advantageously in an aqueous medium, preferably water, or
15 another liquid component of the synthesis mixture. Less preferably they may be added in dry, but not calcined, form. It is believed that calcination significantly reduces the activity of small crystallites to act as seeds; similarly any other treatment that reduces the seeding activity of
20 materials should be avoided.

The colloidal seeds are generally present in the synthesis mixture in a concentration of up to 10000, advantageously at most 3000, more advantageously at most 1500, and preferably at most 1000, more preferably at most
25 500, and most preferably at most 350 ppm, based on the total weight of the synthesis mixture. A minimum seeding level is generally 1 ppb (0.001 ppm), advantageously at least 0.1, more advantageously at least 1, and preferably at least 10, ppm, based on the total weight of the synthesis mixture.
30 Advantageous ranges of proportions are from 1 to 2000, preferably 100 to 1500, and most preferably 100 to 250, ppm.

Apart from the presence of the seeds, the synthesis mixture used is typically one that is known in the art or as described in the literature as suitable for the production of

the molecular sieve concerned. This is also the case for the conditions of treatment, except that the presence of the seeds may make possible the reduction of reaction times or may obviate stirring if that were otherwise necessary.

5 In general, the treatment of the synthesis mixture to yield the desired crystalline molecular sieve, usually termed hydrothermal treatment, though strictly that term should be used only for treatments in which there is vapour-phase water present, is advantageously carried out under autogenous
10 pressure, for example in an autoclave, for example a stainless steel autoclave which may, if desired, be ptfelined. The treatment may, for example, be carried out at a temperature within the range of from 50, advantageously from 90, especially 120, to 250°C, depending on the molecular
15 sieve being made. The treatment may, for example, be carried out for a period within the range of from 20 to 200 hours, preferably up to 100 hours, again depending on the molecular sieve being formed. The procedure may include an ageing period, either at room temperature or, preferably, at a
20 moderately elevated temperature, before the hydrothermal treatment at more elevated temperature. The latter may include a period of gradual or stepwise variation in temperature.

For certain applications, the treatment is carried out
25 with stirring or with rotating the vessel about a horizontal axis (tumbling). For other applications, static hydrothermal treatment is preferred. If desired, the synthesis mixture may be stirred or tumbled during an initial part of the heating stage, for example, from room temperature
30 to an elevated, e.g., the final treatment, temperature, and be static for the remainder. Agitation generally produces a product with a smaller particle size and a narrower particle size distribution than static hydrothermal treatment.

If the product is desired in small particle size form, a larger number of smaller sized LEV seeds is desirably employed. The smaller the mean particle size of the seeds, the lower the weight percentage that is effective. The crystals are advantageously stirred into the synthesis mixture for a time sufficient to provide a uniform dispersion, this time being dependent primarily on the viscosity of the synthesis mixture, and also the scale and type of equipment, but ranging generally from 30 seconds to 10 minutes.

The present invention accordingly provides in a second aspect a process for the manufacture of a crystalline molecular sieve, which process comprises treating a synthesis mixture comprising elements necessary to form the molecular sieve and colloidal LEV crystalline molecular sieve seeds for a time and at a temperature appropriate to form the desired molecular sieve.

As mentioned above, the LEV seed crystals may be used in the manufacture of a molecular sieve of a structure type other than LEV. Such seeding may be regarded as "heterostructural", whereas seeding with seeds of the same structure type is termed "isostructural", whether or not the seeds are of the same composition (i.e., contain the same elements in the same proportions) as the crystalline molecular sieve to be produced.

The present invention accordingly provides in a third aspect a process for the manufacture of a crystalline molecular sieve, which comprises treating a synthesis mixture comprising elements necessary to form a molecular sieve of a first structure type, other than LEV, and colloidal LEV molecular sieve seed crystals for a time sufficient and at a temperature appropriate to form the molecular sieve of the first structure type.

In some embodiments of this aspect, the structure types of the desired molecular sieves are topologically similar to LEV, i.e., are members of the ABC-6 group of materials, as described in Topochemistry of Zeolites and Related Materials, J.V. Smith, Chem. Rev. 1988, 88, 149 at 167, the disclosure of which is incorporated herein by reference. The ABC-6 group includes, *inter alia*, the Offretite and Chabazite, as well as the Levyne, structures. In other embodiments, topologically dissimilar structure types, e.g., MOR, FER, MAZ, EUO, and MFS, are produced.

In further aspects, the invention provides the use, in the synthesis of a crystalline molecular sieve, of colloidal LEV seed crystals to avoid the need for an organic template, to produce different morphologies, or to control the morphology, of the product, to control the purity, particle size or particle size distribution of the product, or to accelerate the formation of the product, or to achieve two or more such effects.

Also as indicated above, colloidal LEV seeds are especially suitable in the manufacture of phosphorus-containing molecular sieves, more especially aluminophosphates and silicoaluminophosphates. They are also especially useful in the manufacture of a colloidal suspension of a crystalline molecular sieve of another structure type, especially CHA.

The invention also provides the products of the processes and of the uses of the earlier aspects of the invention. The products, if required after cation exchange and/or calcining, have utility as catalyst precursors, catalysts, and separation and absorption media. They are especially useful in numerous hydrocarbon conversions, separations and absorptions. They may be used alone, or in admixture with other molecular sieves, in particulate form, supported or unsupported, or in the form of a supported

layer, for example in the form of a membrane, for example as described in International Application WO 94/25151.

Hydrocarbon conversions include, for example, cracking, reforming, hydrofining, aromatization, oligomerisation,

5 isomerization, dewaxing, and hydrocracking (e.g., naphtha to light olefins, higher to lower molecular weight hydrocarbons, alkylation, transalkylation, disproportionation or isomerization of aromatics). Other conversions include the reaction of alcohols with olefins and the conversion of
10 oxygenates to hydrocarbons.

Conversion of oxygenates may be carried out with the oxygenate, e.g., methanol, in the liquid or, preferably, the vapour phase, in batch or, preferably, continuous mode.

When carried out in continuous mode, a weight hourly space
15 velocity (WHSV) based on oxygenate, of advantageously 1 to 1000, preferably 1 to 100, hour^{-1} may conveniently be used. An elevated temperature is generally required to obtain economic conversion rates, e.g., one between 300 and 600°C, preferably from 400 to 500°C, and more preferably about 450°C.
20 The catalyst may be in a fixed bed, or a dynamic, e.g., fluidized or moving, bed.

The oxygenate feedstock may be mixed with a diluent, inert under the reaction conditions, e.g., argon, nitrogen, carbon dioxide, hydrogen, or steam. The concentration of
25 methanol in the feedstream may vary widely, e.g., from 5 to 90 mole per cent of the feedstock. The pressure may vary within a wide range, e.g., from atmospheric to 500 kPa.

The following Examples, in which parts are by weight unless otherwise indicated, illustrate the invention. The
30 source and purity of starting materials are those first given, unless indicated otherwise.

Example 1

This example illustrates the manufacture of a colloidal LEV-type zeolite.

5 In a first stage, 15.95 parts of sodium aluminate (Dynamit Nobel, 53 % Al_2O_3 , 41 % Na_2O , 6 % H_2O), 19.95 parts of sodium hydroxide (Baker, 98.6 %) and 5.58 parts of potassium hydroxide (Baker, 87.4 %) were dissolved in 151.06 parts of water, and heated to boiling until a clear solution
10 was obtained. After cooling to room temperature, water loss was compensated, to form Solution A. 270.60 parts of colloidal silica (Ludox HS40, 40 % SiO_2) were mixed with 106.12 parts of choline chloride (R, Fluka) forming a viscous mass, and Solution A added with stirring at increasing speed
15 as the viscosity decreased, together with 190 parts of rinse water, mixing then continuing for a further 5 minutes. The molar composition was:

1.95 Na_2O :0.24 K_2O :0.46 Al_2O_3 :10 SiO_2 :4.187 R:155 H_2O .

20

To 290 parts of this mixture, 0.49 parts of conventional LEV zeolite seeds were added, and a sample transferred to an autoclave, where it was heated in a 120°C oven for 144 hours. The product was washed, recovered by centrifuging and dried
25 overnight at 120°C. The product comprised spherical aggregates of from 2 to 2.5 μm , made up of ~100 nm particles, with an X-ray diffraction pattern (XRD) of ZSM-45, a zeolite of LEV-type structure, as described in EP-A-107 370 (Mobil).

The product was used as seeds in the next stage, in
30 which 8.38 parts of sodium aluminate, 10.53 parts of sodium hydroxide, 2.96 parts of potassium hydroxide, and 78.95 parts of water were treated as described above to form a Solution A. Solution A was then added to a mixture of 142.42 parts of colloidal silica and 55.5 parts of choline chloride,

together with 100.00 parts of rinse water and mixed as described above, with the addition of 0.68 parts of the first stage seeds. The reaction mixture was heated in an autoclave at 120°C for 174 hours, the product recovered by
5 washing, centrifuging and drying having an XRD similar to that of the first stage. The second supernatant of the washing procedure was not clear, and had a pH of 10.3. It was found to be a dispersion with a solids content of 2.3 %. Analysis by scanning electron microscopy (SEM) and XRD showed
10 ~100 nm crystals with a ZSM-45 structure, LEV structure type.

Example 2

This example illustrates use of a colloidal LEV
15 suspension in the manufacture of a chabasite dispersion suitable for use, in turn, for seeding in SAPO-34 manufacture. The colloidal LEV seeds were prepared as follows:

A synthesis mixture was prepared as described in the
20 first part of Example 1, except that as seeds the colloidal sol from the second supernatant of the second part of Example 1 was used, at a seeding level of 0.15% by weight of solids. The seeded synthesis mixture was heated in a stainless steel autoclave for 96 hours at 120°C, with a heat-up time of 3
25 hours. The product, recovered by centrifuging and drying, had an XRD pattern corresponding to ZSM-45. The first supernatant was not clear and yielded, after centrifuging at 11000 rpm and further washing, a colloidal dispersion with solids content 4.6%, of crystals of size about 100 nm, XRD
30 showing the product to be ZSM-45, a LEV structure-type zeolite.

Solution A was prepared as described in Example 1 using

the following components, in the proportions shown:

	NaOH	61.66
	KOH	28.73
5	Al(OH) ₃ (Alcoa, 99.3 %)	15.73
	H ₂ O	190.30

300.23 parts of colloidal silica and 168.89 parts of water were poured into a mixer, and Solution A added together
10 with 12.65 parts of rinse water. After mixing for 5 minutes, 16 parts of the 4.6 % solids LEV slurry were added. The molar composition of the synthesis mixture was:

3.8 Na₂O:1.12 K₂O:0.5 Al₂O₃:10 SiO₂:161 H₂O,
15 with 927 ppm seeds.

The synthesis mixture was heated in an autoclave to 100°C over 2 hours, and maintained at that temperature for 96 hours. After cooling, the content of the autoclave, a milky
20 suspension, was washed five times with demineralized water and centrifuged at 9000 rpm. After taking a sample for XRD and SEM, the remainder was redispersed to form a colloidal solution, stable over several days, with a solids content of 6.4 %. The XRD of the product shows it to be chabasite,
25 with a uniform particle size 100 x 400 nm.

Example 3

This example illustrates the use of colloidal LEV seeds
30 in the manufacture of SAPO-34 of small particle size and uniform size distribution.

A synthesis mixture was prepared from the following components in the proportions shown.

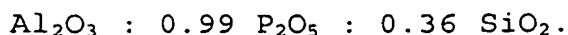
	Solution	Component	Proportion
5	A	Al ₂ O ₃ (Pural SB Condea 75%)	68.18
		H ₂ O	100.02
	B	H ₃ PO ₄ (Acros, 85%)	115.52
		H ₂ O,	80.27
10	C	Colloidal Silica (Ludox AS40)	22.73
		H ₂ O, rinse	10.20
	D	TEAOH (Eastern Chemical, 40%)	182.85
15	E	DPA (Fluka)	80.23
	F	Seeds, 4.6 Wt.% LEV	31.95

20 Slurry A was prepared in a mixer, and Solution B added, when a viscous solution resulted. After leaving the solution to rest for 2 minutes, 26.84 parts of rinse water were added. After mixing the paste for 6 minutes, C was added, and mixed for 2 minutes before adding Solution D. Upon adding E with
25 70.72 parts of rinse water two phases were formed. After a further 3 minutes mixing a visually homogeneous solution resulted and after a further 10 minutes mixing the colloidal seeds F were added. The molar composition was:

30 Al₂O₃:P₂O₅:0.3 SiO₂:TEAOH:1.6 DPA:56 H₂O.
+ 1860 ppm by weight LEV seeds.

The seeded gel was heated for 60 hours at 175°C in a stainless steel autoclave. The solid product was recovered

by centrifugation, washed 11 times with water to a conductivity of about 18 $\mu\text{S}/\text{cm}$, and dried at 120°C. XRD and SEM showed a pure SAPO-34 product with crystals between 0.2 and 1.3 μm , with a few crystals between 2 and 3 μm . Chemical
5 analysis indicated a product of molar composition:

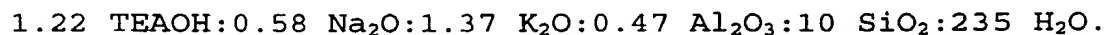


Example 4

10

This example illustrates the use of the colloidal LEV structure type seeds in manufacturing mordenite.

7.20 parts of NaOH, 26.90 parts of KOH (87.3%), 11.32 parts of $\text{Al}(\text{OH})_3$ and 75 parts of water were boiled until a
15 clear solution was obtained, cooled, and water added to compensate for the weight loss on boiling to provide solution A. 229.83 parts of Ludox AS40 were combined with 256.93 parts of water in a beaker, to which was added a solution of 68.70 parts of TEAOH in 100.02 parts of water. Finally
20 solution A was added; rinse water totalling 25.41 parts was also added. A smooth gel resulted, of molar composition:



25 The synthesis mixture was divided, and to one sample, A, a colloidal LEV slurry, contaminated with some OFF, total solids content 4.6 % was added to give a seed level of 201 ppm. The other sample, B, remained unseeded.

Both synthesis mixtures were put into stainless steel
30 autoclaves, and heated to 150°C over 2 hours. Sample A was maintained at that temperature for 96 hours, sample B was maintained at that temperature for 240 hours, with samples being taken at 48 and 96 hours.

After 96 hours, crystals had settled on the bottom of the autoclave containing sample A. XRD and SEM analysis of the product recovered showed MOR, with crystal sizes between 0.2 and 1.0 μm , contaminated by a few OFF needles.

5 The 48 and 96 hours product samples from Sample B were amorphous; the 240 hours product contained MOR crystals of size range between 5 and 10 μm , with amorphous material and OFF needles contamination. The Sample A product analysed:

10 $\text{SiO}_2 : \text{Al}_2\text{O}_3, 15.5 : 1.$

The sample shows that seeding with colloidal LEV accelerates the formation of mordenite and reduces the crystal size.

15

Example 5

This example further illustrates the use of LEV seeds in the manufacture of a non-LEV material, in this case

20 ferrierite.

7.21 parts of NaOH, 26.92 parts of KOH, 11.31 parts of $\text{Al}(\text{OH})_3$ and 75.02 parts of water were boiled until a clear solution was obtained, cooled, and water loss on boiling compensated to provide solution A. 229.87 parts of Ludox
25 AS40 and 407.85 parts of water were poured into the beaker of a mixer and solution A added, together with 14.18 parts of rinse water, and mixed for 10 minutes to provide a smooth gel synthesis mixture of the molar composition:

30 $0.58 \text{ Na}_2\text{O} : 1.37 \text{ K}_2\text{O} : 0.47 \text{ Al}_2\text{O}_3 : 10 \text{ SiO}_2 : 235 \text{ H}_2\text{O}.$

The synthesis mixture was divided, and to one sample, A, the colloidal LEV slurry used in Example 4 was added to give a seed level of 207 ppm. The other part, Sample B, was

unseeded. The samples were hydrothermally treated at the temperatures and times given in Example 4.

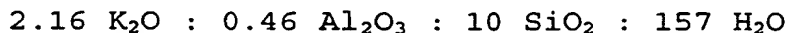
After 96 hours, crystals had settled on the bottom of the sample A autoclave. XRD and SEM analysis of the recovered product showed FER, in flake type crystals of about 2 μm length, contaminated with OFF needles. Chemical analysis gave $\text{SiO}_2 : \text{Al}_2\text{O}_3$ of 15.6 : 1.

The 48 and 96 hours product samples from sample B were amorphous. After 240 hours, the sample B product contained FER crystals in admixture with amorphous material.

The examples show that organic template-free manufacture of ferrierite is accelerated by colloidal LEV crystals, and flake crystals result.

15 Examples 6 to 8

These examples illustrate the use of LEV colloidal seeds to make FER zeolite without the use of an organic template, and the effect of using two different seed concentrations. A template-free synthesis mixture of the following molar concentration was prepared:



25 and divided into three parts, samples A, B and C.

Sample A was unseeded.

Samples B and C (Examples 6 and 7) were seeded with a colloidal LEV seed slurry to levels of 260 ppm (Example 6) and 500 ppm (Example 7). Each sample was placed in a stainless steel autoclave, and heated at 200°C for 96 hours. Unseeded Sample A produced an amorphous product, while both Samples B and C produced the desired FER zeolite. The product of Sample C had a $\text{SiO}_2 : \text{Al}_2\text{O}_3$ molar ratio of 10 : 1. In a similar manner, a seeding level of 1000 ppm was used to

produce, from a synthesis mixture (Example 8) having a molar composition of:

2.16 K₂O : 0.35 Al₂O₃ : 10 SiO₂ : 162 H₂O,

5

a FER zeolite with a SiO₂ : Al₂O₃ molar ratio of 13 : 1.

Example 9

10 This example illustrates the manufacture of FER type product using LEV washwater seeds to accelerate production and avoid the need for an organic template.

7.21 parts of NaOH, 26.92 parts of KOH, 11.31 parts of Al(OH)₃ were dissolved in 75.02 parts of water by boiling and
15 with subsequent water loss compensation to form solution A. Colloidal silica (Ludox AS40), 229.87 parts, was mixed with 407.85 parts of water. Solution A was added, followed by 14.18 parts of rinse water, and the gel stirred for 10 minutes. A LEV washwater dispersion was added, the molar
20 composition of the synthesis mixture then being:

0.58 Na₂O: 1.37 K₂O: 0.47 Al₂O₃: 10 SiO₂: 235 H₂O
plus 207 ppm LEV.

25 The synthesis mixture was heated in an autoclave to 150°C over 2 hours, and maintained at that temperature for a total of 96 hours, after which time crystals had already settled on the vessel bottom. The product was FER, flake type crystals ~2 µm long, slightly contaminated with OFF
30 needles. An unseeded mixture which was also heated to 150°C over 2 hours was still amorphous after 240 hours at 150°C.

Example 10

This example illustrates the use of colloidal LEV seeds to produce a different morphology of FER zeolite.

5 A synthesis mixture of the molar composition:

0.45 Na₂O : 3.1 pyridine : 0.166 Al₂O₃ : 10 SiO₂ : 145 H₂O

was prepared and divided into two parts. One, Sample A, was
10 seeded with sufficient 4.6 % LEV slurry to give a seed level
of 224 ppm. The other part, Sample B, was left unseeded.
Both samples were placed in a stainless steel autoclave and
heated in two hours to 150°C and maintained at 150°C for 140
hours. The unseeded product was largely amorphous, with
15 traces of ZSM-5. The LEV-seeded product was pure ZSM-35, a
FER structure type zeolite, with a flat plate-like
morphology.

Example 11

20

This example illustrates the effect of seeding level on particle size of FER.

A synthesis mixture similar to that of Example 1, first stage, was prepared, having a molar composition as follows:

25 1.95 Na₂O : 0.23 K₂O : 0.46 Al₂O₃ : 10 SiO₂ : 4.15 choline
chloride : 157 H₂O.

This mixture was divided, to one sample, A, were added
sufficient colloidal LEV seed slurry prepared as in Example 3
to give a seeding level of 200 ppm, while the other sample,
30 B, had a seeding level of 600 ppm.

Each sample was heated at 150°C for 48 hours. The
products, analysed by XRD and SEM, were identified as ZSM-38,
a FER-type zeolite, as described in U.S. Patent No. 4 046
859. In both cases, the crystals were intergrown plates,

with the crystal size depending on seeding level; 600 ppm giving a mean crystal size of 0.7 μm , while 200 ppm gave a mean crystal size of 1.0 μm .

5 Example 12

This example illustrates the use of colloidal LEV seeds to produce a Linde Zeolite T, of type structure ERI/OFF, and to control the morphology of the product.

10 The synthesis mixture used in Examples 6 to 8 was seeded with 200 ppm of the LEV slurry used there, and hydrothermal treatment carried out at 120°C instead of the 200°C used in those examples. The product was a disk-like crystallite of an intergrowth of ERI/OFF zeolite, known as Linde Zeolite T,
15 as described in U.S. Patent No. 4 126 813.

Example 13

This example illustrates the control of particle size by
20 seeding with LEV in the manufacture of a MAZ structure type zeolite. 32.38 parts of NaOH (98.6%) and 22.71 parts of $\text{Al}(\text{OH})_3$ (98.5%) were dissolved in 63.37 parts of water by boiling, the solution cooled, and water loss compensated to form solution A. 17.60 parts of tetramethyl ammonium
25 chloride (TMACl, 98%) were dissolved in 24.04 parts of water at room temperature in a high shear mixer and 218.78 parts of colloidal silica (Ludox HS-40, 40%) added with stirring over 2 minutes, then 5.38 parts of a 4.6% aqueous colloidal LEV solution, prepared as in Example 3, added and mixed for 3
30 minutes. Solution A was then added with 27.19 parts rinse water, and stirred in for 5 minutes, to give a paste-like gel with a molar composition of:

2.74 Na_2O : 0.98 Al_2O_3 : 1.1 TMACl: 10 SiO_2 : 101 H_2O

35 with 600 ppm LEV seeds.

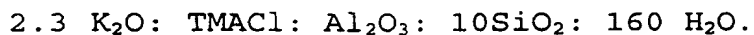
380 parts of gel were heated in a plastic bottle fitted with a condenser in a 98°C oilbath for 135 hours. The resulting product was washed five times with 700 parts of water to a pH of 10.9, the product dried at 120°C (yield 89.5 parts) and calcined in air for 24 hours at 510 to remove the TMA, weight loss 9.2%. Product yield: 21.4%, XRD analysis showed an excellently crystalline TMA-MAZ and SEM showed uniform 500 nm spherical agglomerates consisting of nanocrystallites.

An unseeded but otherwise identical synthesis mixture subjected in the same hydrothermal treatment yielded a TMA-MAZ product slightly contaminated with TMA-sodalite, formed of spherical particles with a broad size distribution (about 0.3 to 2.5 μm).

Example 14 and Comparative Example 15

These examples illustrate the use of colloidal LEV seeds in controlling the particle size of offretite.

A synthesis mixture was prepared using TMACl as the template and Ludox AS40 as silica source. The molar composition was:



25

One sample (Example 14) was seeded to a level of 202 ppm using a 4.6% solids content dispersion of colloidal LEV (see Example 3). The mixture was heated in an autoclave at 150°C for 8 hours. The product was pure OFF, with crystals having a narrow size distribution, about 1 μm . The second sample, (Comparison Example 15), was left unseeded, and heated at 150°C for 48 hours. The product was pure OFF, with particles sizes ranging between 1 and 5 μm .

Example 16 and Comparative Example 17

These Examples illustrate the use of colloidal LEV seeds to control purity and particle size in ZSM-57 manufacture.

5 A synthesis mixture was prepared using N,N,N,N',N',N' hexaethylpentane diammonium bromide (R) as template, Ludox HS 40 as silica source, and $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ as alumina source. The molar composition was:

10 R: $2\text{Na}_2\text{O}$: 0.17 Al_2O_3 : 10 SiO_2 : 399.4 H_2O

A first sample (Example 16) seeded with 175 ppm colloidal LEV was heated at 160°C for 144 hours. The product was fully crystalline ZSM-57, with particle size about 1 μm .

15 A second sample (Comparison Example 17) was left unseeded, and heated at 160°C. Crystallization did not start until 14 days. After 24 days the product was a mixture of ZSM-57, quartz and other crystalline phases, the ZSM-57 material was platelets of about 3 μm diameter, mixed with
20 other crystallites.

Examples 18 and 19

These Examples illustrate the use of colloidal LEV seeds
25 in the manufacture of a FER type zeolite, ZSM-38.

A synthesis mixture was prepared using sodium aluminate (Nobel, 53% Al_2O_3 , 41% Na_2O) as the alumina source, Ludox HS 40 as the silica source and choline chloride (R, Aldrich) as template. The mixture had the molar composition:

30

1.95 Na_2O : 0.24 K_2O : 0.46 Al_2O_3 : 10 SiO_2 : 4.17R: 157 H_2O

One sample was used unseeded, a second (Example 18) was seeded with a 4.6% solids content dispersion of colloidal LEV

to a 200 ppm loading. Both samples were heated in autoclaves at 150°C. After 71 hours the unseeded sample was still amorphous. After 48 hours, the seeded sample had produced ZSM-38, an FER structure type zeolite (see U.S. Patent No. 4 5 046 859), crystal size (intergrown plates) about 1.0 µm.

A third sample (Example 19) was similarly seeded but to a loading of 0.06%. After being similarly heated, the product was similar to that of Example 18, but the crystal size was smaller, at about 0.7 µm.

10

Example 20

This example illustrates the effect of colloidal LEV and colloidal *BEA in the synthesis of ZSM-50 (structure type 15 EUO). The use of colloidal LEV reduces the crystallization time needed under static conditions compared to a synthesis mixture seeded with colloidal *BEA of 80 nm particle size.

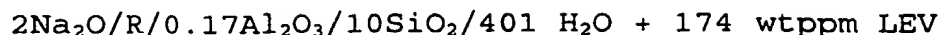
A solution A was prepared using the following ingredients in the proportions indicated:

20

Al ₂ (SO ₄) ₃ .18H ₂ O	18.98
NaOH (98.7%)	27.59
H ₂ O	150.06

25 225.06 parts of colloidal silica (Ludox HS40) and 765.01 parts of water were poured together and mixed. Solution A was added using 21.38 parts of rinse water. After mixing, solution B, consisting 61.57 parts of hexamethonium bromide (R) in 100.49 parts of water was added using 20.82 parts of 30 rinse water. To 798.64 parts of the mixture which was homogenized were added 3.032 parts of the 4.6 Wt.% colloidal slurry of LEV of Example 3. The final homogeneous mixture

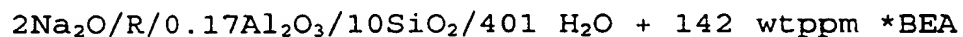
with the following molar composition:



5 was transferred to a 1 litre stainless steel autoclave and heated to 150°C over 6 hours. Heating was continued for 168 hours. The sample was washed and dried and XRD and SEM showed ZSM-50, elliptical plates of length 1µm.

A mixture with composition

10



was prepared and crystallized in the same way as above. A sample was taken after 168 hours of heating at 150°C. XRD
15 showed very poor crystallinity. After 216 hours of heating the crystallinity of the recovered product increased. The product was fully crystalline ZSM-50 after 312 hours.

Example 21

20

This example illustrates the use of LEV seeds in isostructural seeding, to accelerate the formation of LEV (ZSM-45).

A synthesis mixture was prepared as described in the
25 first part of Example 1, except that instead of seeding with conventionally sized LEV seeds, the colloidal sol from the second supernatant of the second part of Example 1 was used, at a seeding level of 0.15% by weight of solids. The seeded synthesis mixture was heated in a stainless steel autoclave
30 for 96 hours at 120°C, with a heat-up time of 3 hours. The product, recovered by centrifuging and drying, had an XRD pattern corresponding to ZSM-45. The first supernatant was not clear and yielded, after centrifuging at 11000 rpm and further washing, a dispersion with solids content 4.6%. The

product consisted of crystals of size about 100 nm, XRD showing ZSM-45.

It can be seen that the use of washwater seeds, rather than regular sized seeds, reduces the synthesis time from 144 to 96 hours. This example also illustrates the formation of washwater seeds.

Example 22

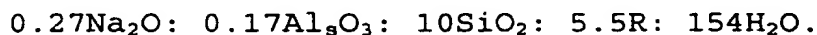
10 This example illustrates the use of the washwater seeds of Example 21 to accelerate the formation of LEV (ZSM-45).

Following the procedures of Example 21 and the first part of Example 1, a synthesis mixture was prepared, but seeded with the washwater seeds of Example 21 at a level of 15 0.02% by weight of solids. The synthesis mixture was heated at 120°C and spot samples taken at intervals were washed, recovered by centrifuging and drying, and subjected to XRD analysis. Crystallization had begun at 24 hours, and was complete after 48 hours. The XRD pattern of the product 20 corresponds to that of ZSM-45.

Example 23

This example illustrates the use of the washwater seeds 25 of Example 21 to accelerate the formation of LEV (NU-3).

A solution of 0.75 parts sodium aluminate (53% Al_2O_3 , 42% Na_2O , 6% H_2O), 0.61 parts NaOH, and 161.06 parts of diethyldimethyl ammonium hydroxide (R, 20.4% in water) was made up, and added to 33.35 parts of silica (90%) with 2 30 parts of rinse water, and mixed for 10 minutes to give a low viscosity gel of molar composition:



To 120.58 parts of this mixture were added sufficient of the washed suspension of Example 21 to give a seeding level of 0.15% by weight, while the remainder of the mixture was
5 left unseeded.

Both samples were treated in autoclaves for 96 hours at 130°C. While the unseeded product was very slightly hazy, it was still transparent and no product could be recovered. The seeded product contained a blue-white mother liquor and a
10 solid phase on the autoclave base. After washing and drying the solid was observed by XRD analysis to have the pattern of NU-3 (a zeolite of LEV structure type) as set out in EP-A-40016. The particles were non-aggregated and had a particle size about 100 nm.

15

Example 24

This example illustrates the use of LEV seeds to accelerate NU-3 formation.

20 6.35 parts of alumina (Catapal VISTA, 70%) were slurried in 19.99 parts of water. Quinuclidine (R, 97%), 7.2 parts, and NH_4F , 8.11 parts, were dissolved in 50.02 parts of water, and 7.2 parts of H_2SO_4 (97%) added dropwise with stirring. 29.01 parts of silica were placed in a mixer and the alumina
25 slurry added, together with 15.02 parts rinse water. At very slow mixing speed, the slurry gelled the silica, and the quinuclidine solution was added with 35.81 parts of rinse water. The viscous gel was mixed for 5 minutes, to give a molar composition of:

30

$1.6\text{H}_2\text{SO}_4$: $5\text{NH}_4\text{F}$: Al_2O_3 : 10SiO_2 : 5.3R : $161\text{H}_2\text{O}$.

To 102 parts of this gel was added sufficient washwater seed suspension from Example 21 to give a seed loading of

0.06% by weight based on the total weight of the gel. The remainder was left unseeded. Both samples were heated at 170°C for 192 hours. The products were washed and recovered by centrifuging and dried overnight at 120°C. The unseeded product was amorphous while the seeded product had the XRD pattern of NU-3, and SEM showed intergrown crystals of various morphology, of between 0.5 and 1.5 μm .

Example 25

10

This example illustrates the use of the washwater seeds of Example 21 to accelerate zeolite formation and to control particle size and increase purity of ZSM-45 (LEV).

9.08 parts of sodium aluminate (as Example 2), 11.56 parts NaOH, and 3.10 parts KOH were dissolved in 85.75 parts of water by boiling and water loss compensated, to give solution A. Silica, 68.69 parts, was combined with water, 85.70 parts, and 60 parts choline chloride, and mixed at low speed. Then solution A was added, with 80.82 parts of additional water. The stirring speed was increased, and stirring continued for a further 5 minutes.

The washed suspension of Example 21 was added to part of the mixture to give a seeding level of 0.02% by weight, and a further part was left unseeded. Both samples were heated at 120°C for 96 hours, and samples taken, product recovered, and dried overnight at 120°C. In the seeded sample, the XRD pattern was that of ZSM-45, consisting of spherical 1 μm aggregates built up of 100 nm particles. In the unseeded mixture, crystallisation had only just started; the mixture was subjected to a further 96 hours heating at 120°C. The product recovered was an impure ZSM-45, consisting of 6 μm aggregates.

CLAIMS:

1. A colloidal suspension of a LEV structure type crystalline molecular sieve.

5

2. A suspension as claimed in claim 1, wherein the mean size of the LEV particles is within the range of from 5 to 1000 nm.

10 3. A suspension as claimed in claim 2, wherein the range is from 10 to 300 nm.

4. A suspension as claimed in claim 3, wherein the range is from 20 to 100 nm.

15

5. A suspension as claimed in claim 1, wherein the mean size of the LEV particles is at most 100 nm.

6. A method for preparing a suspension as claimed in any preceding claim, which comprises synthesizing a LEV structure type crystalline molecular sieve by treatment of a synthesis mixture containing the elements necessary to form a LEV crystalline molecular sieve, separating the resulting LEV crystalline molecular sieve product from the synthesis mixture, washing the product, and recovering the resulting wash liquid.

20

25

7. A method as claimed in claim 6, wherein the recovered wash liquid is the liquid resulting from the second or subsequent washing.

30

8. The product of the method of claim 6 or claim 7.

9. Colloidal LEV crystals when recovered from a suspension as claimed in any one of claims 1 to 5 or prepared by a method as claimed in claim 6 or claim 7 and separation from the wash liquid.

5

10. A process for the manufacture of a crystalline molecular sieve, which process comprises treating a synthesis mixture comprising elements necessary to form the molecular sieve and colloidal LEV crystalline molecular sieve seeds for a time
10 and at a temperature appropriate to form the desired molecular sieve.

11. A process as claimed in claim 10, wherein the desired molecular sieve is of the LEV structure type.

15

12. A process as claimed in claim 11, wherein the desired molecular sieve is Levyne, ZK-20, NU-3 or ZSM-45.

13. A process for the manufacture of a crystalline molecular
20 sieve, which comprises treating a synthesis mixture comprising elements necessary to form a molecular sieve of a first structure type, other than LEV, and colloidal LEV molecular sieve seed crystals for a time sufficient and at a temperature appropriate to form the molecular sieve of the
25 first structure type.

14. The invention as claimed in claim 11, in which colloidal LEV structure type seeds are used in the manufacture of a crystalline molecular sieve of the MFS, CHA, OFF, MOR, FER,
30 MAZ, EUO or ERI/OFF, structure type.

15. A process as claimed in claim 14, wherein the crystalline molecular sieve manufactured is chabasite, a phosphorus-containing molecular sieve of the CHA structure

type, mordenite, ferrierite, Linde Zeolite T, mazzite, offretite, ZSM-57, ZSM-38, or ZSM-50.

16. The use, in the synthesis of a crystalline molecular sieve other than of LEV structure type by thermal treatment of a synthesis mixture suitable for the manufacture of that molecular sieve, of colloidal LEV seed crystals to control the morphology of the product.

17. The use as claimed in claim 16, wherein colloidal LEV seeds are used to form Linde Zeolite T of disk-like morphology.

18. The use, in the synthesis of a crystalline molecular sieve, of colloidal LEV seed crystals to control a characteristic of the resulting crystalline molecular sieve.

19. The use as claimed in claim 18, wherein the characteristic is the purity, the particle size, or the particle size distribution.

20. The use in the synthesis of a crystalline molecular sieve of colloidal LEV seed crystals to facilitate manufacture of the molecular sieve in the substantial absence of an organic structure-directing agent, or to accelerate the formation of the product.

21. The crystalline molecular sieve produced by the process or use claimed in any one of claims 10 to 20.

22. The crystalline molecular sieve of claim 21, in a chemical form suitable for use as a catalyst or a separation or absorption medium.

23. A hydrocarbon conversion, separation, or absorption carried out using a sieve as claimed in claim 22.

24. An oxygenate conversion using a sieve as claimed in
5 claim 22.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 99/02468

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C01B37/08 C01B39/26 C01B39/30 C01B39/44 C01B39/46
C01B39/48 B01J29/04 B01J20/18 C10G3/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01B B01J C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 98 16469 A (EXXON CHEMICAL PATENTS INC) 23 April 1998 (1998-04-23) page 5, line 14 -page 7, line 2 ---	1,10-12
A	US 4 495 303 A (KUEHL GUENTER H) 22 January 1985 (1985-01-22) claims 1,4 column 3, line 60 -column 4, line 18 column 6, line 40 -column 8, line 40 ---	1,10-12, 18-24
A	EP 0 107 370 A (MOBIL OIL CORP) 2 May 1984 (1984-05-02) claims 1,12 page 7, line 11 -page 8, line 23 page 1, line 1 - line 3 page 6, line 24 - line 27 --- -/--	1,10-12, 18-24



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Rigondaud, B

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 99/02468

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>EP 0 110 650 A (MOBIL OIL CORP) 13 June 1984 (1984-06-13) page 3, line 5 - line 7 page 5, line 1 - line 4 page 10, line 17 - line 20 -----</p>	6

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 99/02468

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9816469 A	23-04-1998	AU 5147498 A EP 0951444 A	11-05-1998 27-10-1999
US 4495303 A	22-01-1985	AU 574739 B AU 3570984 A BR 8406053 A CA 1232596 A DK 563484 A EP 0147034 A JP 60145910 A	14-07-1988 06-06-1985 03-09-1985 09-02-1988 30-05-1985 03-07-1985 01-08-1985
EP 0107370 A	02-05-1984	AU 566767 B AU 1919883 A BR 8305274 A CA 1204718 A DK 439283 A NZ 205613 A ZA 8307204 A JP 59078923 A US 5334367 A	29-10-1987 05-04-1984 02-05-1984 20-05-1986 28-03-1984 11-06-1986 29-05-1985 08-05-1984 02-08-1994
EP 0110650 A	13-06-1984	AU 564738 B AU 2151183 A BR 8306419 A CA 1213576 A DK 531283 A, B, JP 1776025 C JP 4063010 B JP 59131521 A NZ 206295 A ZA 8308722 A	27-08-1987 31-05-1984 26-06-1984 04-11-1986 23-05-1984 28-07-1993 08-10-1992 28-07-1984 10-09-1986 31-07-1985